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XIX.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF
HARVARD COLLEGE.

ON THE CUPRIAMMONIUM DOUBLE SALTS.

SECOND PAPER.

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THE continuation of the study of the cupriammonium double salts, begun in 1891,* has led to the preparation of the following new compounds:—

- (1.) $\text{Cu}(\text{NH}_3)_2\text{ClCHO}_2$.
- (2.) $\text{Cu}(\text{NH}_3)_3\text{BrC}_2\text{H}_3\text{O}_2 \cdot \text{H}_2\text{O}$.
- (3.) $\text{Cu}(\text{NH}_3)_2\text{BrC}_3\text{H}_5\text{O}_2$.
- (4.) $\text{Cu}(\text{NH}_3)_2\text{BrC}_3\text{H}_5\text{O}_3$.
- (5.) $\text{Cu}(\text{NH}_3)_2\text{ClC}_3\text{H}_5\text{O}_3$.

(1.) CUPRIAMMONIUM FORMIOCHLORIDE, $\text{Cu}(\text{NH}_3)_2\text{ClCHO}_2$.

The bromide corresponding to this chloride has been described already by Richards and Shaw. The chloride itself was obtained at the same time by these experimenters, but only in an impure state, and the present problem was to determine the conditions necessary for the preparation of the substance in a state of purity.

If any considerable amount of water is present in the materials, basic salts of copper are certain to be precipitated, and to contaminate the preparation. On the other hand, the slight solubility of cupric formiate and cupriammonium chloride in alcohol makes it difficult to avoid the admixture of these substances with the desired compound, if alcohol is used in the anhydrous condition.

* Theo. W. Richards, *Berichte d. d. ch. Gesell.*, XXV. 1492; T. W. Richards and H. G. Shaw, *These Proceedings*, XXVIII. 247.

The following procedure was found to be the most successful, but great care was needed to carry it out. Three grams of crystallized cupric formiate were dissolved in just enough warm alcohol to effect solution, and two grams of ammoniac chloride were added to the mixture. The whole was then heated to boiling, and dry ammonia was passed in until a very slight excess was present. Upon cooling and evaporation in the air, fine blue prismatic crystals separated, which were fairly pure, as the analyses show. The salt resembles in its properties the formiobromide, being permanent in dry air, but at once decomposed by water. In color it is a purer blue than the formiobromide, having much less of the greenish tinge.

In the analysis of the compound the copper was determined electrolytically after the substance had been evaporated with sulphuric and nitric acids. The chlorine from a new portion was weighed as argentic chloride, and the ammonia was distilled after the addition of potash. The formic acid was determined by combustion.

Analyses of $\text{Cu}(\text{NH}_3)_2\text{ClCHO}_2$.

- I. 0.0862 gram of the substance gave on electrolysis 0.0305 gram of copper.
- II. 0.0997 gram of the substance gave on electrolysis 0.0356 gram of copper.
- III. 0.1258 gram of the substance yielded 0.0994 gram of argentic chloride.
- IV. 0.1285 gram of the substance yielded 0.1008 gram of argentic chloride.
- V. 0.1060 gram of the substance distilled with caustic potash required 11.75 cubic centimeters of a decinormal solution for neutralization.
- VI. 0.0984 gram of the substance yielded on combustion 0.0241 gram of carbon dioxide.

Analyses III. and IV. were made from different samples; hence they prove the definiteness of the compound.

	Copper.	Ammonia.	Chlorine.	Formic Acid.
I. . .	35.38			
II. . .	35.71			
III. . .	—	—	19.54	
IV. . .	—	—	19.40	
V. . .	—	18.91		
VI. . .	—	—	—	25.05
Averages	35.54	18.91	19.47	25.05

	Calculated for $\text{Cu}(\text{NH}_3)_2\text{ClCHO}_2$.	Found.
Copper	35.69	35.54
Ammonia	19.15	18.91
Chlorine	19.90	19.47
Formic Acid (CHO_2)	25.26	25.05
	100.00	98.97

(2.) AMMON-CUPRIAMMONIUM ACETOBROMIDE,
 $\text{Cu}(\text{NH}_3)_3\text{BrC}_2\text{H}_3\text{O}_2 \cdot \text{H}_2\text{O}$.

This compound is formed readily when cupric bromide is dissolved in a mixture of alcohol and glacial acetic acid, and an excess of dry ammonia gas is passed into the solution. It is essential to have the solutions concentrated. For example, 2.5 grams of cupric bromide were shaken with 13 cubic centimeters of glacial acetic acid and 25 cubic centimeters of alcohol. Upon cooling after the addition of the ammonia, which raised the temperature of the solution, the desired substance separated out. If when passing in the gas a black precipitate ($\text{Cu}_3\text{Br}_6(\text{NH}_3)_{10}$) falls after the solution has become dark purple,* the supernatant liquid should be decanted before it is allowed to crystallize. The precipitate shows the presence of an excess of cupric bromide in proportion to the acetic acid.

Ammon-cupriammonium acetobromide had already been made by Richards and Shaw; but the analyses of the compound were so unsatisfactory that no account of the substance was given in their paper. This unsatisfactoriness was due, not to any difficulty in preparing the

* Richards and Shaw, *loc. cit.*

substance in a state of purity, as in the previous instance, but rather to the great difficulty of drying the substance enough without drying it too much. The extra molecule of ammonia and the molecule of water are held very loosely, mere exposure to the air allowing them to escape. Especially is this the case when the substance is placed over sulphuric acid. 0.1242 gram of material, which had been exposed thus until constant in weight, yielded 0.0331 gram, or 26.65 per cent, of copper upon electrolysis. This showed that the substance had lost practically all of its extra ammonia and water, for the theoretical per cent of copper in $\text{Cu}(\text{NH}_3)_2\text{BrC}_2\text{H}_3\text{O}_2$ is 26.87. The new salt consists of pearly flakes of a brilliant light blue color, somewhat less intense than that of the normal cupriammonium acetobromide. It is only very slightly soluble in alcohol, and is at once decomposed by water, a little of the copper going into solution. In properties and general appearance it resembles the ammon-cupriammonium acetochloride prepared by Richards and Shaw, except that it is much less stable.

The acetic acid was determined by distillation with phosphoric acid, according to the well known method of Fresenius. Hydrobromic and a trace of phosphoric acid which come over in the distillate were precipitated with argentic nitrate from the neutralized solution, the result being calculated as argentic bromide, since this is the greater part of the precipitate.

Analyses of $\text{Cu}(\text{NH}_3)_3\text{BrC}_2\text{H}_3\text{O}_2 \cdot \text{H}_2\text{O}$.

- I. 0.3276 gram of the substance yielded 0.0774 gram of copper upon electrolysis.
- II. 0.3902 gram of the substance yielded 0.0896 gram of copper upon electrolysis.
- III. 0.3376 gram of the substance yielded 0.2365 gram of argentic bromide.
- IV. 0.2453 gram of the substance yielded 0.1732 gram of argentic bromide.
- V. 0.4214 gram of the substance yielded 0.2940 gram of argentic bromide.
- VI. 0.2600 gram of the substance distilled with caustic potash required 13.28 cubic centimeters of a decinormal acid solution for neutralization.
- VII. 0.1528 gram of the substance distilled with caustic potash required 16.29 cubic centimeters of a decinormal solution for neutralization.

VIII. The distillate from a mixture of 0.1469 gram of the substance with phosphoric acid required 5.67 cubic centimeters of a decinormal alkali for neutralization. Approximately corrected for the alkalimetric equivalent of the argentic phosphate and bromide obtained from the distillate, this amount becomes 5.47 c.c.

	Copper.	Ammonia.	Bromine.	C ₂ H ₃ O ₂ .
I. . .	23.63			
II. . .	22.97			
III. . .	—	—	29.81	
IV. . .	—	—	30.04	
V. . .	—	—	29.68	
VI. . .	—	18.20		
VII. . .	—	18.19		
VIII. . .	—	—	—	22.35
Averages .	23.30	18.20	29.84	22.35

	Calculated for above Formula.	Found.
Copper	23.40	23.30
Ammonia	18.84	18.19
Bromine	29.42	29.84
Acetic Acid	21.72	22.35
Water (by difference)	6.62	6.32
	<u>100.00</u>	<u>100.00</u>

It is evident that most of the substance analyzed had lost some of its ammonia and water. A few other determinations were made of substance just prepared and not dried at all, in order to be sure that the atomic ratio of the ammonia to the copper was not greater than 3 : 1. This point was proved beyond a doubt.

(3.) CUPRIAMMONIUM PROPIONOBROMIDE, Cu(NH₃)₂BrC₃H₅O₂.

Ten grams of ammonic propionate, made by neutralizing propionic acid with ammonia gas and allowing the solution to evaporate over caustic potash, were mixed with two grams of cupric bromide, and

dissolved in about fifty cubic centimeters of absolute alcohol. Dry ammonia gas was passed into the solution, and on standing a precipitate of cupriammonium bromide ($\text{Cu}(\text{NH}_3)_2\text{Br}_2$) came down. Four and a half cubic centimeters of strong propionic acid were added to dissolve the precipitate, and more ammonia gas was added. Again the same crystals appeared, showing that the tendency to form this substance was much more decided than the tendency to form the substance desired. Since the addition of more propionic acid did not help the matter, one and a half grams of precipitated cupric oxide were added, and the whole was warmed until most of the powder had dissolved. After filtration and evaporation in the air, prismatic crystals of a very strong blue color were deposited, proving to be the substance sought. The crystals were washed with alcohol, and dried in the air, in which they are permanent. 0.5750 gram of the substance was found to displace 0.2197 gram of toluol having a specific gravity of 0.8619; hence the specific gravity of cupriammonium propionobromide is 2.255. The other properties resemble so closely those of the acetic compound that it is not worth while to detail them.

Analyses of $\text{Cu}(\text{NH}_3)_2\text{BrC}_3\text{H}_5\text{O}_2$

- I. 0.1017 gram of the substance gave on electrolysis 0.0262 gram of copper.
- II. 0.1061 gram of the substance gave on electrolysis 0.0270 gram of copper.
- III. 0.0825 gram of the substance yielded 0.0624 gram of argentic bromide.
- IV. 0.0788 gram of the substance distilled with caustic potash required 6.19 cubic centimeters of a decinormal acid for neutralization.
- V. 0.1109 gram of the substance yielded 0.0588 gram of carbon dioxide upon combustion.

	Copper.	Ammonia.	Bromine.	Propionic Acid.
I. . . .	25.76			
II. . . .	25.45			
III. . . .	—	—	32.18	
IV. . . .	—	13.40		
V. . . .	—	—	—	29.31
Averages .	25.60	13.40	32.18	29.31

	Calculated for above Formula.	Found.
Copper	25.37	25.60
Ammonia	13.61	13.40
Bromine	31.90	32.18
Propionic acid	29.12	29.31
	<hr/> 100.00	<hr/> 100.49

(4.) CUPRIAMMONIUM LACTOBROMIDE, $\text{Cu}(\text{NH}_3)_2\text{BrC}_3\text{H}_5\text{O}_2$.

This compound is easily obtained by dissolving syrupy lactic acid and about a third of its weight of cupric bromide in alcohol, and then passing dry ammonia gas into the solution. Basic salts of copper do not form readily here, but if an insufficiency of lactic acid is added, $\text{Cu}(\text{NH}_3)_2\text{Br}_2$ will crystallize out. The crystals are of a strong light blue color, with a faint tinge of purple; they may be obtained of great size. They are permanent in the air, and at once decomposed by water. 2.6377 grams of the substance were found to displace 1.0334 grams of toluol, indicating a specific gravity of 2.20.

For analysis the salt was washed twice with alcohol, and pressed between filter paper.

Analyses of $\text{Cu}(\text{NH}_3)_2\text{BrC}_3\text{H}_5\text{O}_2$.

- I. 0.1742 gram of the substance gave on electrolysis 0.0418 gram of copper.
- II. 0.1108 gram of the substance yielded 0.0786 gram of argentic bromide.
- III. 0.1916 gram of the substance yielded 0.1360 gram of argentic bromide.
- IV. 0.0850 gram of the substance required on distillation 6.25 cubic centimeters of decinormal acid solution for neutralization.
- V. 0.0987 gram of the substance required 7.38 cubic centimeters of decinormal acid.
- VI. 0.1634 gram of the substance yielded on combustion 0.0819 gram of carbon dioxide.

Analyses II. and III. were made from different samples of the substance.

	Copper.	Ammonia.	Bromine.	Lactic Acid. C ₃ H ₅ O ₃ .
I. . . .	23.99			
II. . . .	—	—	30.19	
III. . . .	—	—	30.20	
IV. . . .	—	12.56		
V. . . .	—	12.84		
VI. . . .	—	—	—	33.79
Averages .	23.99	12.70	30.19	33.79

	Calculated for above Formula.	Found.
Copper	23.85	23.99
Ammonia	12.79	12.70
Bromine	29.99	30.19
Lactic Acid	33.37	33.79
	100.00	100.67

(5.) CUPRIAMMONIUM LACTOCHLORIDE, Cu(NH₃)₂ClC₃H₅O₃.

Four grams of cupric lactate were dissolved in strong alcohol, and when the solution was boiling, two grams of ammonic chloride were added. Through this solution perfectly dry ammonia gas was passed until slightly in excess. Upon filtering and evaporating the solution fine crystals of cupriammonium lactochloride were deposited. A similar method would have answered in the case of the bromine. These crystals are of a somewhat lighter blue color than the lactobromide, but otherwise their properties are similar. Because of this similarity, determinations of the chlorine and copper were considered enough to identify the compound.

Analyses of Cu(NH₃)₂ClC₃H₅O₃.

- I. 0.1751 gram of the substance gave on electrolysis 0.0496 gram of copper.
- II. 0.1341 gram of the substance gave on electrolysis 0.0382 gram of copper.
- III. 0.1314 gram of the substance gave on electrolysis 0.0378 gram of copper.

IV. 0.1025 gram of the substance yielded 0.0659 gram of argentic chloride.

V. 0.1015 gram of the substance yielded 0.0656 gram of argentic chloride.

	I.	II.	III.	IV.	V.
Copper	28.33	28.49	28.76		
Chlorine	—	—	—	15.93	15.98
Average	28.52			15.95	
Calculated for above formula	28.64			15.96	

Attempts were made to make similar compounds of butyric acid without success. Various different proportions, suggested by those required in the previous preparations, were tried with equal failure, and the attempts were finally discontinued.

It was also hoped that such compounds as $\text{Cu}(\text{NH}_3)_2\text{ClNO}_3$ and $\text{Cu}(\text{NH}_3)_2\text{NO}_3 \cdot \text{C}_2\text{H}_3\text{O}_2$ might be found. The results of a great many experiments showed that under ordinary conditions nothing but $\text{Cu}(\text{NH}_3)_2\text{Cl}_2$ or $\text{Cu}(\text{NH}_3)_4(\text{NO}_3)_2$ can be obtained. Further attempts to combine cupriammonium sulphate with cupriammonium acetate were also unsuccessful; so that in these directions the field seems to be limited. All of these facts, as well as the relative properties of those compounds which have been prepared, may be of some use in the future when the structure of the cupriammonium compounds comes under consideration. Work upon the subject, as well as upon similar investigation of products containing amines instead of ammonia, is being continued here.

CAMBRIDGE, MASS., September 20, 1894.